

DRAFT

Development of a Total Maximum Daily Load for Dioxin for the Ohio River

Ohio River Miles 237.5 to 317

June 2000

EXECUTIVE SUMMARY

In 1997, the U.S. Environmental Protection Agency, Region 3, entered into a Federal Consent Order to complete a Total Maximum Daily Load (TMDL) for dioxin for the Ohio River by September, 2000. The Ohio River Valley Water Sanitation Commission is completing the monitoring, modeling and daily load analysis on behalf of Region 3. This effort has been coordinated and reviewed, on an ongoing basis, by the Commission's TMDL Work Group. This work group is composed of representatives from all mainstem states, and US EPA Regions 3, 4, 5 and headquarters.

TMDLs are required for waters not meeting applicable water quality standards after application of best practicable control technology. A TMDL must be designed to meet water quality standards, which is 0.013 pg/L for the Ohio River for 2,3,7,8-TCDD (dioxin). TMDLs must include allocations. TMDLs must consider background conditions, which are accounted for through the utilization of the dioxin sample data. TMDLs must consider critical conditions and seasonality, which are accounted for by utilizing harmonic mean flow.

Based on West Virginia's 1998 303(d) list, a dioxin TMDL is to be completed for the Ohio River segment from Ohio River Mile (ORM) 237.5 to ORM 317. This segment borders Ohio and West Virginia. "High Volume" dioxin sampling, a collection technique that effectively concentrates 1000 liters (L) into a single sample in order to achieve necessary detection levels, was conducted within the TMDL segment during 1997-1998. Multiple samples were collected over the period at various flows. The data are used to estimate TMDL segment boundary loads and to verify water quality modeling results. The SMPTOX4 water quality model was utilized to determine dioxin loads at various river flows. The model was run at three flows: seven day-ten year low flow, harmonic mean flow, and a one-year flood high flow. These flow regimes compare reasonably with flows at which monitoring data were collected. Modeling results cannot be reliably verified at flows substantially above the one-year flood due to uncertainties that cannot be evaluated due to the absence of monitoring data at higher flows.

Based on monitoring and modeling data, the Ohio River frequently exceeds both Ohio's and West Virginia's water quality standard for dioxin within the TMDL segment at all flows evaluated. West Virginia's water quality standards apply a 10^{-6} CRL (0.013 pg/L for dioxin) at 7Q10 low flow, while Ohio's standards apply a 10^{-5} CRL (0.13 pg/L) at one-tenth harmonic mean flow (equivalent to a 10^{-6} CRL at harmonic mean flow).

The highest dioxin concentrations and loads in the Ohio River occur immediately downstream of the Kanawha River at ORM 266. The harmonic mean flow was selected as the appropriate critical condition for use with the dioxin stream criterion which has been established to protect human health at a 10^{-6} cancer risk level over life-time exposures to ingestion of water and fish. The harmonic mean flow most accurately describes long-term flow conditions. At this flow, model results indicate a total daily maximum load of 2,3,7,8-TCDD in the Ohio River equal to 4248 ug/day. The load that would not result in stream criterion exceedances at this flow equals 1097 ug/day. Thus, a 74 percent reduction in the dioxin load is necessary. Eighty one percent of the total Ohio River dioxin loading is from the Kanawha River Basin and the remaining 19 percent from the upper Ohio River Basin.

Based on monitoring data and modeling results, Ohio River dioxin concentrations increase with increasing flow. At the one-year flood, modeled dioxin concentrations and loads at ORM 266 are 0.13 pg/L and 83,693 ug/day, respectively. The stream criterion and resulting load that would not cause water quality standards violations at the one-year flood flow condition are 0.013 pg/L and 8491 ug/day, respectively. Thus, Ohio River loads would need to be reduced by ninety percent to meet water quality standards at the one-year flood. At the one-year flood, 55 percent of the total dioxin loading originates within the Kanawha River Basin, while the remaining 45 percent is from the upper Ohio River Basin. It is anticipated that loadings would be even greater at higher flows.

There is no net increase of dioxin within the TMDL segment except for Kanawha River inputs, thus all important dioxin sources are located upstream of the TMDL segment. While several contaminated sites have been identified in the Kanawha Basin, no dioxin loads to surface waters within or upstream of the Ohio River TMDL segment have been identified. Potential higher flow-related sources include runoff from contaminated sites and re-suspension of contaminated bed sediments. Atmospheric deposition was eliminated as a source within the TMDL segment based on results of limited sampling, however it could be a source upstream of the TMDL segment. Results of an upper-Ohio River dioxin survey (Figure 10) suggest the possibility of sources upstream of ORM 20 and between ORM 129 and 175.

A monitoring plan to identify and quantify sources in the upper-Ohio River and to quantify loads from re-suspension of contaminated sediments is presented and will be completed during 2000-01 under the Ohio River Watershed Pollutant reduction Program.

INTRODUCTION

Section 303(d) of the Clean Water Act requires states to develop lists of waters still requiring total maximum daily loads (TMDLs). In 1997, U.S. EPA entered into a federal Consent Agreement obligating them to complete a TMDL for dioxin on the Ohio River from ORM 266 to ORM 312, per West Virginia's 1996 draft 303(d) List, by September, 2000. West Virginia's 1998 303(d) List includes the Ohio River for dioxin (2,3,7,8-TCDD) from Racine Dam at Ohio River mile (ORM) 237.5 to the West Virginia state line at ORM 317. The listing was based on West Virginia fish consumption advisories and "high volume" water column sampling for dioxin conducted by the Ohio River Valley Water Sanitation Commission (ORSANCO). Hence, the

requirement for the Ohio River dioxin TMDL was extended to include the segments on the 1998 list (ORM 237.5 to ORM 317).

The seven minimum regulatory requirements of a TMDL are:

1. TMDLs must be designed to meet water quality standards.
2. TMDLs must include load allocations (LAs) and wasteload allocations (WLAs). A load allocation is an allowable pollutant discharge quantity for a nonpoint source(s). A WLA is an allowable pollutant discharge quantity from a point source(s). The combined WLA and LA must not result in water quality standards violations.
3. TMDLs must consider background (natural) contributions.
4. TMDLs must consider critical conditions.
5. TMDLs must consider seasonal variations (i.e. multiple critical conditions are possible).
6. TMDLs must include a margin of safety.
7. TMDLs must include public participation.

* A revised regulation on TMDLs is currently (99-Aug) in draft and has additional requirements.

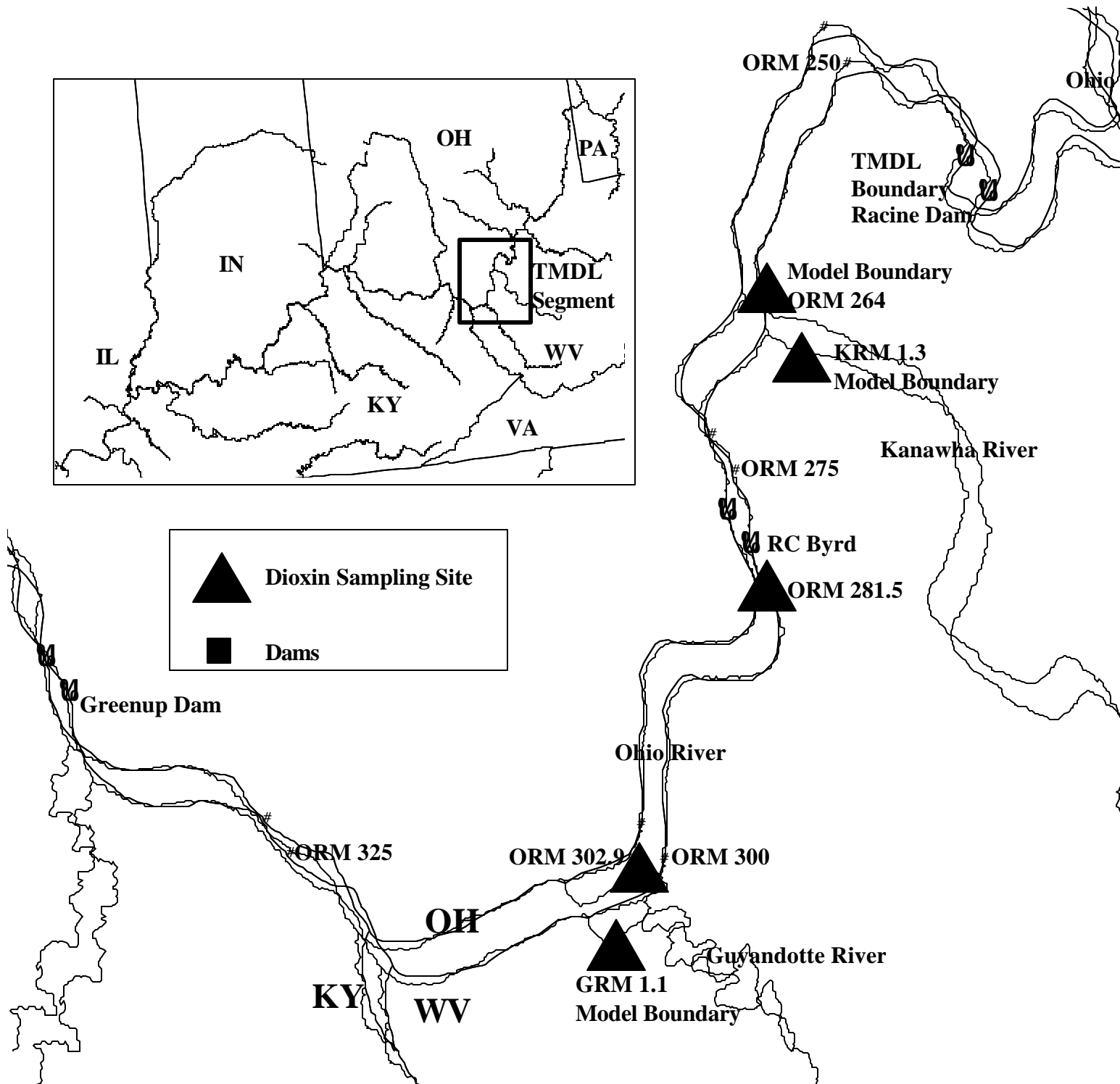
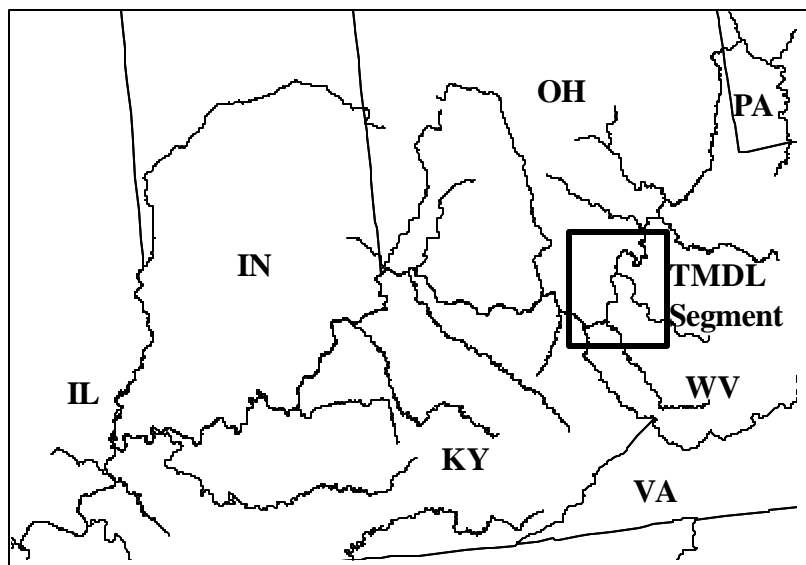
Figure 1 provides a map of the TMDL segment including important land marks and high volume sampling sites used in the TMDL analysis. The TMDL includes a 79.5 mile segment of the Ohio River from Racine Dam (ORM 237.5) to the West Virginia-Kentucky border (ORM 317). This segment forms a portion of the Ohio-West Virginia state border and ends immediately upstream of the Kentucky border. The RC Byrd Dam splits the TMDL segment at ORM 279.2. The Ohio River Basin drains approximately 40,000 square miles upstream of the TMDL segment.

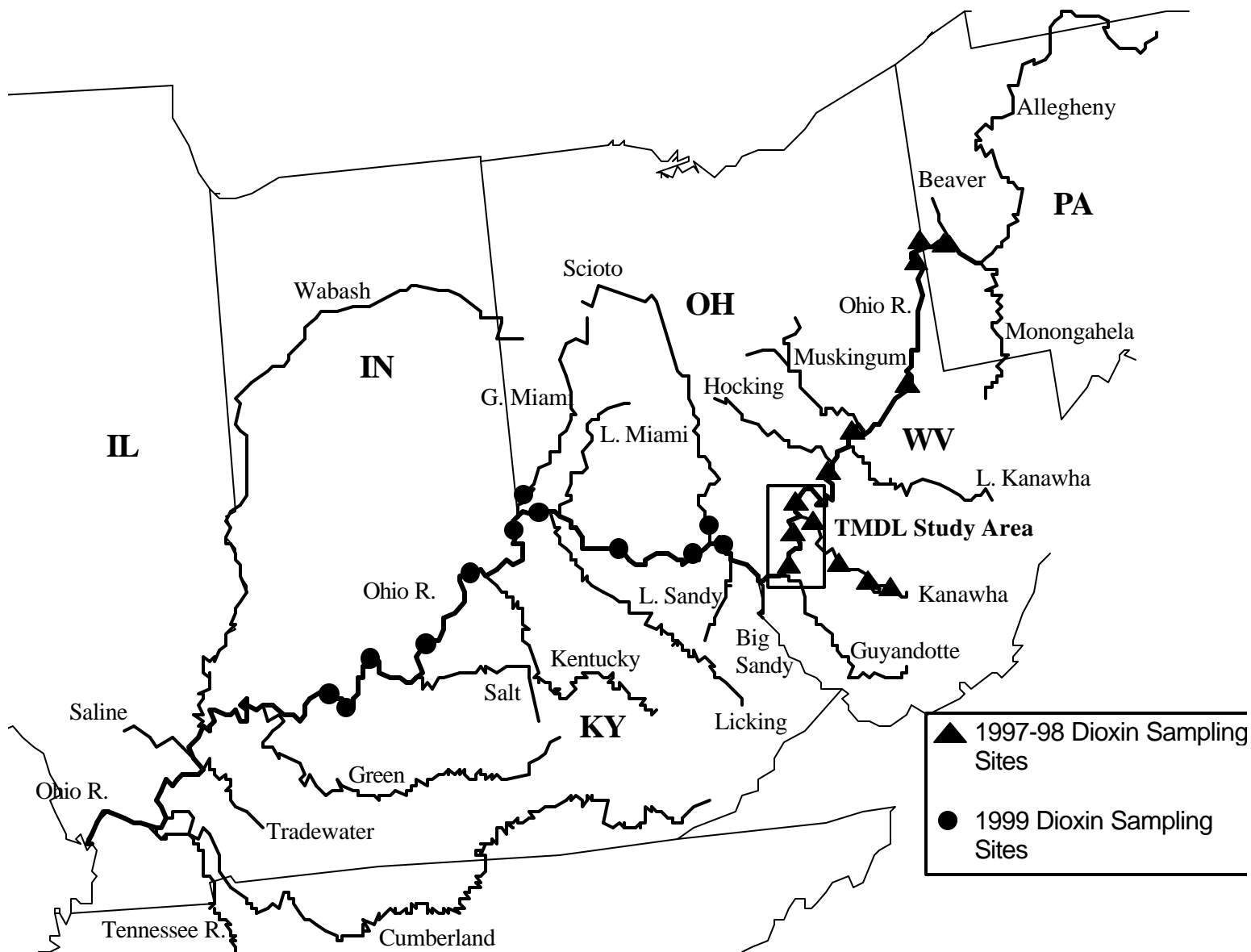
Major tributaries entering the Ohio River within the segment include the Kanawha and Guyandotte Rivers. The Kanawha River contributes approximately one-quarter of the total flow in the Ohio River at the point of confluence and therefore carries a significant potential to affect Ohio River water quality. The Kanawha River drains approximately 12,000 square miles. The Guyandotte River has lesser flow and corresponding lesser potential to affect the Ohio River and drains an area of approximately 1700 square miles. There are an additional four tributaries within the segment with drainage areas ranging from 150 to 700 square miles (Leading Cr., Raccoon Cr., Symmes Cr., Twelvepole Cr.) and a multitude of smaller tributaries.

METHODOLOGY

Water Quality Monitoring Data and Assessment

The Ohio River Valley Water Sanitation Commission collected dioxin samples at sites within the Ohio River TMDL segment, to define boundary conditions (conditions entering the TMDL segments), and at sites upstream of the TMDL segment to define upstream dioxin concentrations. Figure 2 contains a map with locations of all dioxin river sampling locations within the basin. Dioxin samples are collected using a “high volume” method that concentrates 1000 liters (L) of water, effectively lowering the analytical detection level 1000 times. Appendix A contains all sample results for 2,3,7,8-TCDD. Table 1 contains a summary of dioxin monitoring sites and results within or at the boundaries of the TMDL segment for samples collected between June





1997 and November 1998 (data collected upstream of the TMDL segment are presented in Figure 10 later in this report).

Table 1. Summary of Dioxin Data Within the TMDL Segment

River/Site	No. Samples	No. Violations	Max. Conc. Total 2,3,7,8-TCDD, pg/L	Min. Conc. Total 2,3,7,8-TCDD, pg/L
Ohio RM 264	5	2	0.0710	0.0068
Kanawha RM 1.3	7	7	0.4628	0.0941
Ohio RM281.5	5	5	0.1364	0.0240
Ohio RM 302.9	5	5	0.1671	0.0229
Guyandotte RM 1.1	2	1	0.0201	<0.0010

The data indicate frequent water quality standards violations for 2,3,7,8-TCDD in the Ohio River below the confluence with the Kanawha River, which carries a heavy loading of 2,3,7,8-TCDD. Figure 3 presents high volume dioxin sampling results at RC Byrd Dam. The Ohio River above the Kanawha River also violates water quality standards at higher flows.

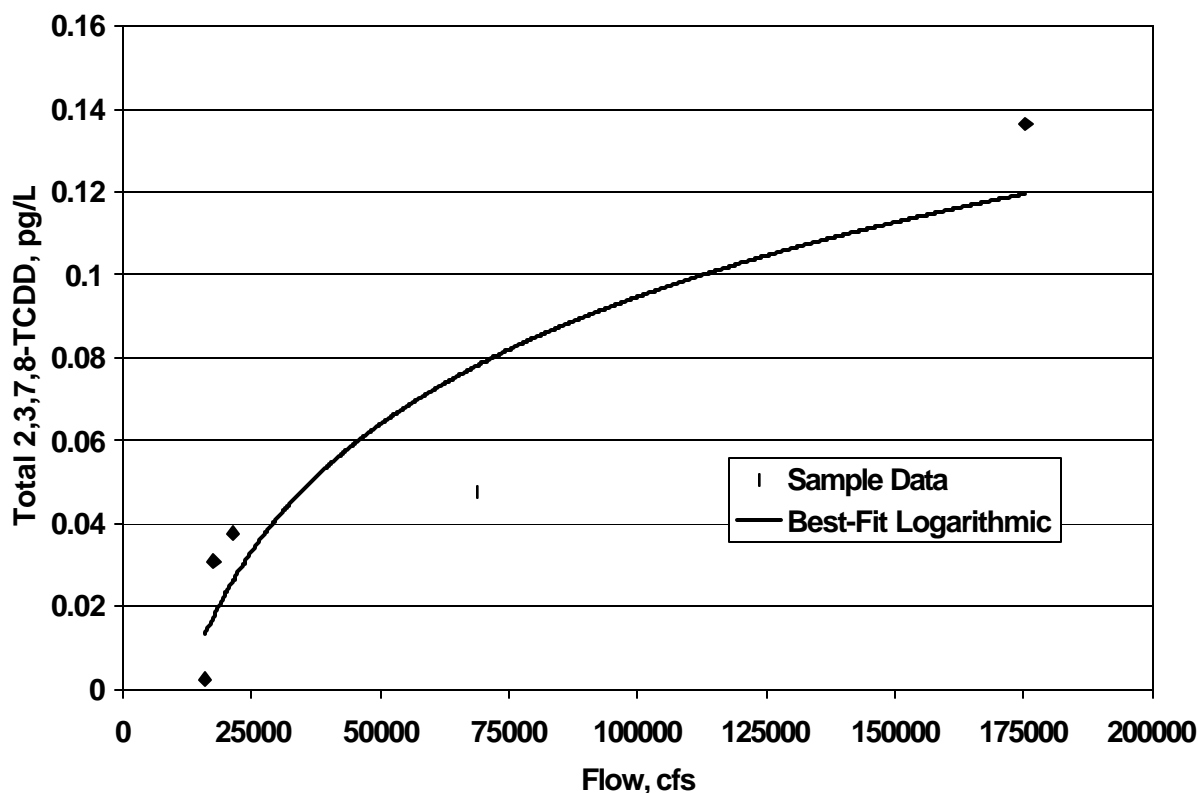


Figure 3. Total Dioxin Vs. Flow at RC Byrd Dam

Water Quality Standards Endpoint

Since the portion of the Ohio River, for which this TMDL is being established, forms the boundary between Ohio and West Virginia, both states' Water Quality Standards for 2,3,7,8-TCDD (dioxin) must be considered in the development of this TMDL. The State of Ohio's Water Quality Standard for the Ohio River is 0.13 pg/L, to be applied at one-tenth the harmonic mean flow, at a cancer risk level (CRL) of 10^{-5} . Surrounding States WQS also should be considered for consistency. Pennsylvania's Water Quality Standard for dioxin is 0.01 pg/L to be applied at harmonic mean flow, and Kentucky's Water quality standard is 0.013 pg/L at harmonic mean flow.

West Virginia's criteria for dioxin is 0.013 pg/L, however, West Virginia Water Quality Standards Regulations (WV-46-1-8-2.b) defer a final decision on critical flow for carcinogens, in order that the State may further study the issue. Presently, the West Virginia Water Quality Standards Regulations state -- "the regulatory requirement for determining effluent limits for carcinogens shall remain as they were on the date this Rule was proposed." WV 46-1-7.2.b states -- in the absence of any special application, numeric water quality standards shall apply at all times when flow is greater than 7Q10 flow.

In this TMDL application, where only load allocations will be developed, we believe that harmonic mean flow is not inconsistent with West Virginia Water Quality Standards Regulations 46 CSR 1. Because human health criteria assume long-term chronic exposure, harmonic mean flow is the most appropriate flow to describe the critical condition. A coordinated and consistent approach among bordering states has become more important, especially for waters like the Ohio River that are shared.

Selection of Critical Condition and Seasonality

Concurrently with selection of a numeric endpoint, in this case the Water Quality criteria, TMDLs need to define the environmental condition that will be used when defining allowable loads. TMDLs are usually designed around the concept of "critical condition". The critical condition is defined as the set of environmental conditions, which, if controls are designed to protect, will ensure attainment of standards for all other conditions.

Because 2,3,7,8-TCDD is defined as a carcinogen, harmonic mean flow has been specifically identified as the appropriate flow condition to use with the criterion (EPA Guidance 1991). Dioxin sources on the Ohio River are believed to arise from a mixture of sources. There may be no other single condition that is protective for all other conditions. For this reason, this TMDL does examine an entire range of flow conditions and can define a load allocation that will be protective for different flows. However, for this TMDL harmonic mean flow is the flow condition that will be used for setting allocations.

Seasonality is inherently accounted for in using the harmonic mean flow, since that flow theoretically accounts for conditions over a long period of time.

Model Selection and Segmentation

After reviewing several models for possible use in performing this TMDL analysis, SMPTOX 4 was selected. SMPTOX is a steady-state flow model that simulates transport and fate of chemical pollutants and sediments. The primary purpose of the model is to determine the maximum dioxin loading within the TMDL segment at critical conditions. SMPTOX was determined to be the most appropriate model considering the transport and fate processes to be simulated, the available data for input to the model, and the most appropriate level of complexity. A comprehensive description of the modeling effort is attached in a separate report, Technical Support Document for the Development of an Ohio River Total Maximum Daily Load for 2,3,7,8-TCDD (Dioxin).

The US Army Corps of Engineers' HEC-2 reservoir hydraulic model was used to determine river segmentation and channel geometry for SMPTOX. River flows and downstream water surface elevation are input to HEC-2. Hec-2 then determines cross-sectional profiles from which cross-sectional areas can be calculated for each river segment. The Ohio River was divided into 16 segments within SMPTOX varying in length from less than one mile to over seven miles. These segments were determined based on changes longitudinally in river cross-sectional area and velocity determined with HEC-2.

Determination of Boundary Conditions

Model boundaries include the Ohio River at ORM 264 (upstream of the Kanawha River), the Kanawha River, and the Guyandotte River. The upstream model boundary at ORM 264 differs from the upstream boundary of the TMDL segment at ORM 237.5. The model boundary at ORM 264 coincides with a high volume dioxin sampling location and is assumed to be representative of the upstream TMDL segment boundary. This difference between the locations of the modeling and TMDL boundaries occurred in part because the TMDL segment was extended from ORM 264 to ORM 237.5 after the modeling effort was initiated. It was decided that there was no reason to extend the model upstream to the upper boundary of the TMDL segment since it is believed that ORM 264 would be representative of conditions at ORM 237.5.

Boundary inputs to be determined include flow, sediment concentrations, and dioxin concentrations. Sediment and dioxin concentrations at input boundaries to the TMDL segment are estimated using high volume survey results. Dioxin and sediment concentrations are known for several flow conditions and are estimated at other flow conditions (including high flow conditions) using a best-fit model. Figure 4 provides particulate dioxin concentrations versus flow along with the best-fit model for the Kanawha River boundary. The same is shown in Figure 5 for the Ohio River upstream TMDL segment boundary at ORM 264. At critical conditions, the *particulate* dioxin concentration is determined from the best-fit model, and the *average dissolved* dioxin concentration is added to it to calculate total dioxin at the boundaries. More detail on this procedure can be found in the modeling report.

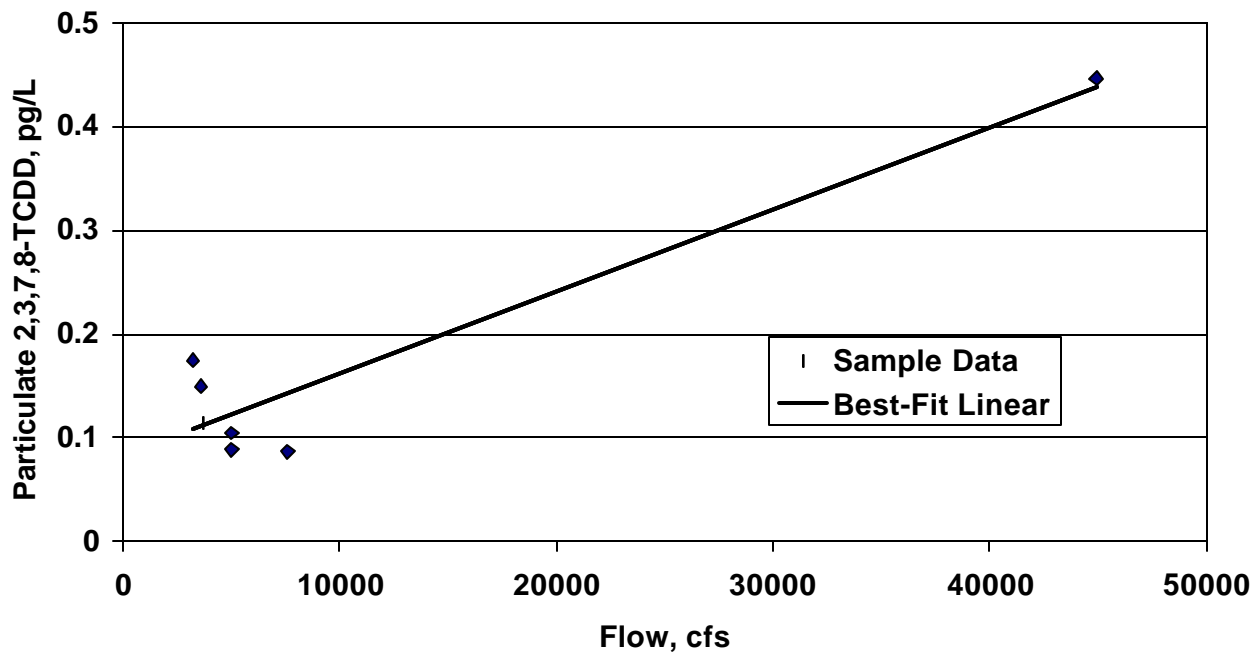


Figure 4. Kanawha River Boundary – Particulate Dioxin Vs. Flow

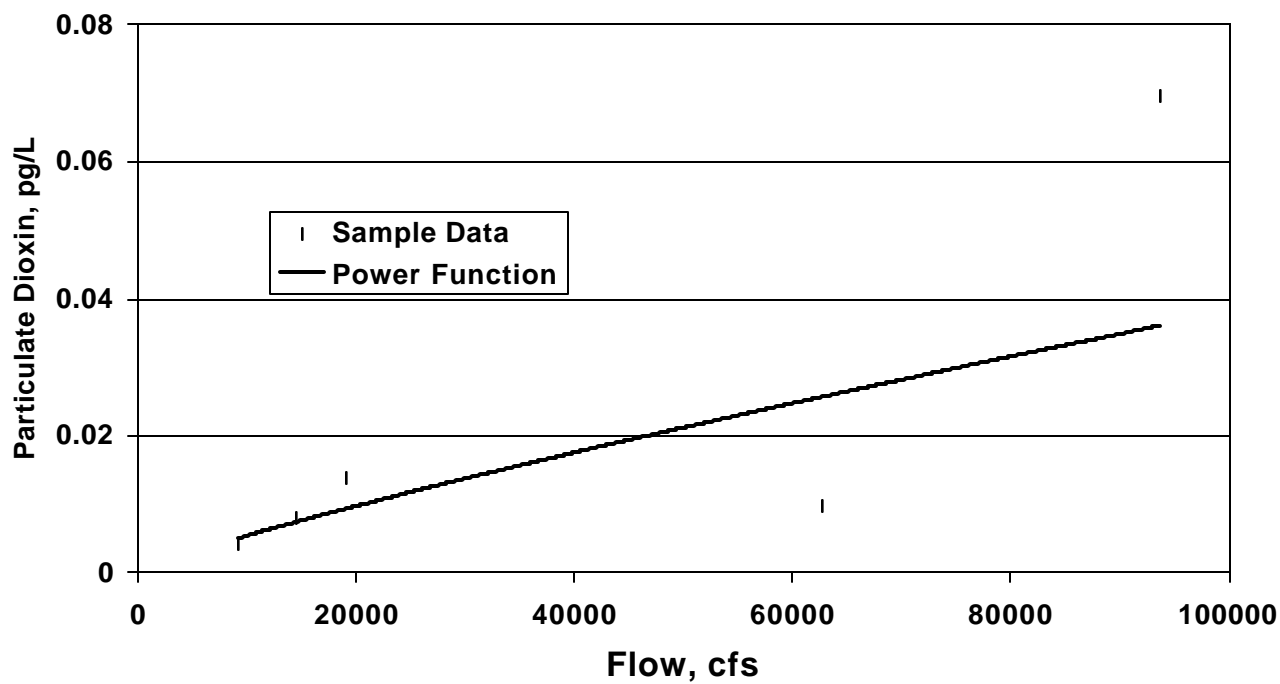


Figure 5. Ohio River TMDL Upstream Boundary – Particulate Dioxin Vs. Flow.

Estimation of Model Variables

In addition to boundary inputs, a number of other model variables were developed as described in detail in the Technical Support Document. More important variables include sediment settling and resuspension velocities and partition coefficient. These variables were developed with the aid of field measurements. Longitudinal suspended solids surveys were conducted for the express purpose of developing settling and resuspension velocities.

RESULTS

Total Maximum Daily Load Analysis

In order to illustrate the variation in dioxin at different flow conditions, the model was executed at three flows: seven-day/ten-year low flow, harmonic mean flow, and at the one-year flood. These flows represent low, moderate, and high flow conditions respectively, with the harmonic mean flow being specified as the critical condition, or the condition under which allocations would be applied. Dioxin concentrations based on model results are presented graphically in Figure 6.

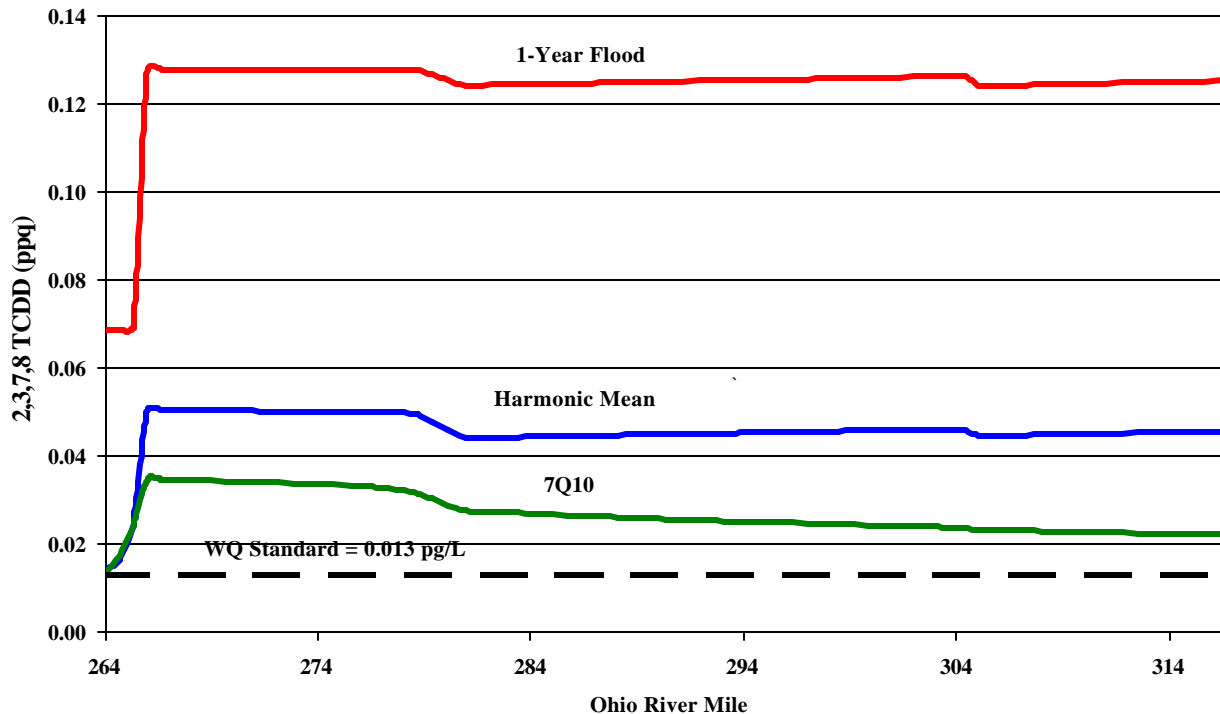


Figure 6. SMPTOX4 Model Results at Various Flows.

ORM 266 (critical river location) is the location on the Ohio River with the highest dioxin concentrations and loads, at all flow conditions modeled, and is positioned immediately downstream of the confluence with the Kanawha River. The water quality standard of 0.013 pg/L is violated at all three flows, at this critical river location, but are highest during the high flow, one-year flood. The maximum modeled concentration of total 2,3,7,8-TCDD is 0.128 pg/L (parts per quadrillion), which occurred immediately downstream of the Kanawha River at ORM 266, the critical location.

Figure 7 plots modeled dioxin loads at low, moderate and high flows at ORM 266. A best-fit power function trend line having an r-squared value of 0.9988 can be used to estimate Ohio River dioxin loads at flows other than those modeled. The equation for the best-fit power function trend line is $y=0.0023x^{1.3917}$ (y in pg/L; x in cfs) which can be used to calculate a predicted dioxin load for any flow. The total 2,3,7,8-TCDD load (modeled) at the critical location in the Ohio River (ORM 266), at the critical harmonic mean flow, is 4248 ug/day. The dioxin total maximum daily load, or the highest load that would not result in violation of the 0.013 pg/L water quality standard at the harmonic mean flow (listed as capacity in Table 2), is 1097 ug/day. Therefore, a 74 percent reduction would be needed to meet water quality standards at the critical harmonic mean flow condition. The Ohio River upstream of the Kanawha River accounts for approximately nineteen percent of the total dioxin load, at the harmonic mean flow, while the Kanawha River accounts for the remaining 81 percent of the dioxin load.

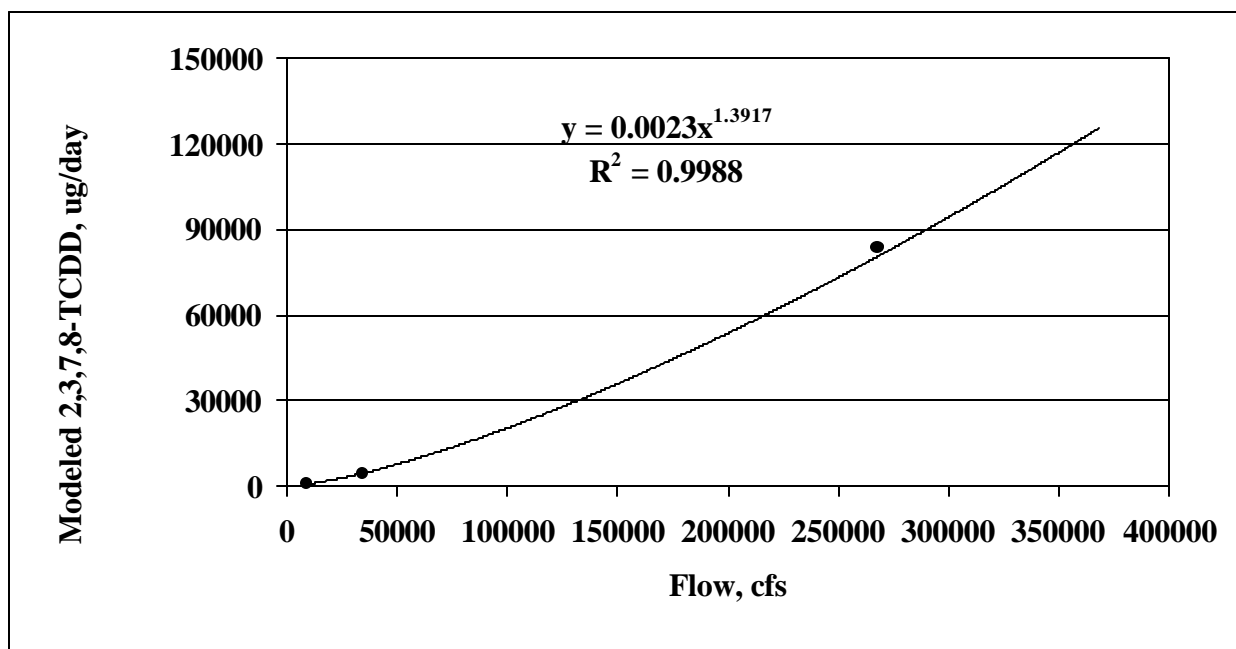


Figure 7. Dioxin Loads at Low, Moderate, and High Flows in the Ohio River at ORM 266

At the one-year flood flow condition, the maximum modeled total dioxin load in the Ohio River is 83,693 ug/day, while the river capacity at that flow is 8,513 ug/day. Therefore, at the one-year flood high flow condition, a 90 percent reduction of the total dioxin load would be necessary not to exceed the water quality criterion. At the high flow, the Ohio River upstream of the Kanawha River accounts for approximately 45 percent of the total Ohio River dioxin load, while the Kanawha River accounts for the remaining 55 percent. The Guyandotte River does not have a measurable affect on dioxin levels in the Ohio River. In fact, based on modeling results, Ohio River dioxin concentrations downstream of the Guyandotte River decrease since the dilution from the Guyandotte River has a greater affect than its dioxin loading. Table 2 provides the percent load reductions for dioxin necessary to meet water quality standards at the seven-day, ten-year low flow, harmonic mean flow, and one-year flood high flow at various locations. Figure 8 shows percent load reductions necessary to meet water quality standards for the Ohio River at the upstream boundary of the TMDL segment and at the worst-case location on the Ohio River immediately downstream of the Kanawha River.

Table 2. 2,3,7,8-TCDD Reductions Necessary to Meet Ohio River Dioxin WQSs.

	Flow cfs	Conc., pg/L	Capacity ug/day	Loading ug/day	% Reduction to Achieve Ohio R.WQS
7Q10 Low Flow					
Ohio R.Upstream of Kanawha R.	6700	0.00524	213	86	0
Kanawha R.	2420	0.11731	77	694	89
Ohio R. Downstream Of Kanawha R., ORM 266	9120	0.03507	290	774	63
Guyandotte R.	180	0.00054	6	0	0
Harmonic Mean Flow					
Ohio R.Upstream of Kanawha R.	26000	0.01260	827	801	0
Kanawha R.	8500	0.16595	270	3451	92
Ohio R. Downstream Of Kanawha R., ORM 266	34500	0.05052	1097	4248	74
Guyandotte R.	1400	0.00111	45	4	0
One-Year Flood					
Ohio R.Upstream of Kanawha R.	225000	0.06868	7155	37803	81
Kanawha R.	42700	0.43955	1358	45914	97
Ohio R. Downstream Of Kanawha R., ORM 266	267700	0.12818	8513	83693	90
Guyandotte R.	6000	0.01586	191	233	0

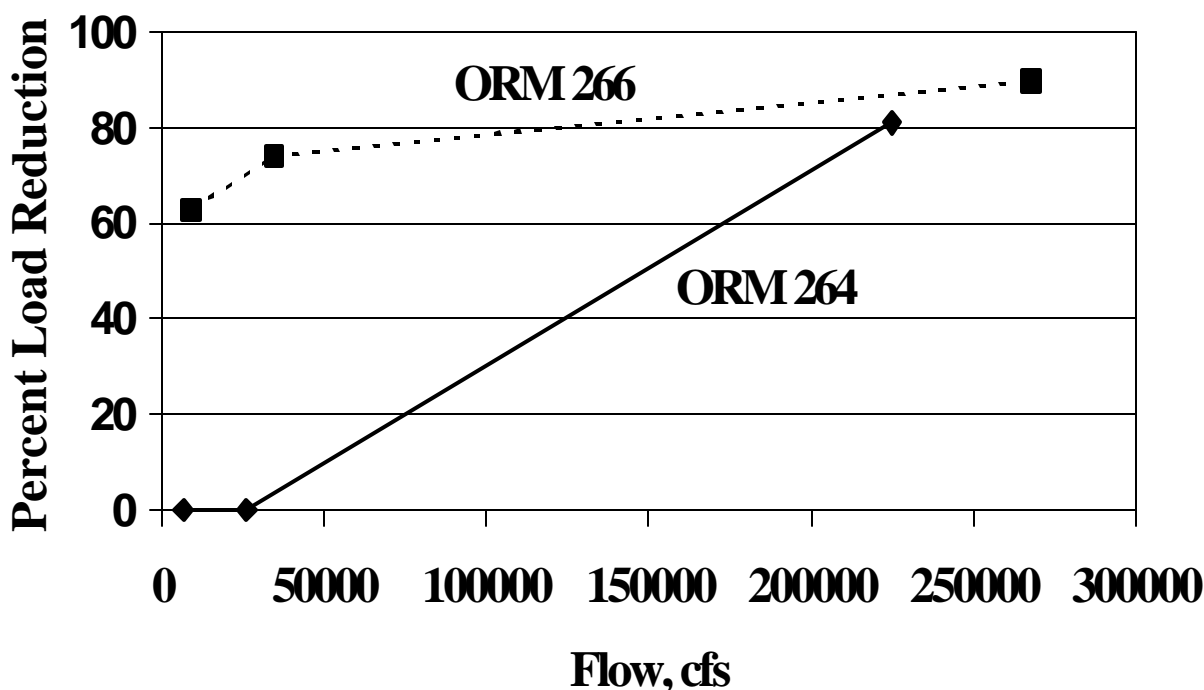


Figure 8. Ohio River Dioxin Load Reductions Necessary to Meet Water Quality Standards at Various Flows.

Margin of Safety

The applicable ambient water quality criterion for 2,3,7,8-TCDD is 0.013 pg/L which is based on a 10^{-6} cancer risk level. This criterion is designed to protect human health from long-term (lifetime) exposure. The harmonic mean flow is theoretically representative of an average flow over a lifetime. The recommended use of the long-term harmonic mean flow for carcinogens has been derived from the definition of the human health criteria (HHC) for carcinogenic pollutants. The adverse impacts of carcinogenic pollutants is estimated in terms of life-time intake. Therefore, estimation of the load reduction necessary to achieve water quality standards for dioxin at the harmonic mean flow will be protective of human health and provide an intrinsic margin of safety. The estimated Ohio River reduction in loading of 2,3,7,8-TCDD, at 7Q10 flow, at the critical point downstream from the Kanawha River, based on the model is 63 percent. The estimated load reduction using the harmonic mean flow at the same location is 74 percent. Therefore, load allocations designed to meet this critical condition of harmonic mean flow would provide an increased margin of safety over 7Q10 for the protection of human health over a lifetime exposure.

Source Assessment

Very little is known about specific source contributions of dioxin to the Ohio River TMDL segment. Potential sources can be categorized as follows:

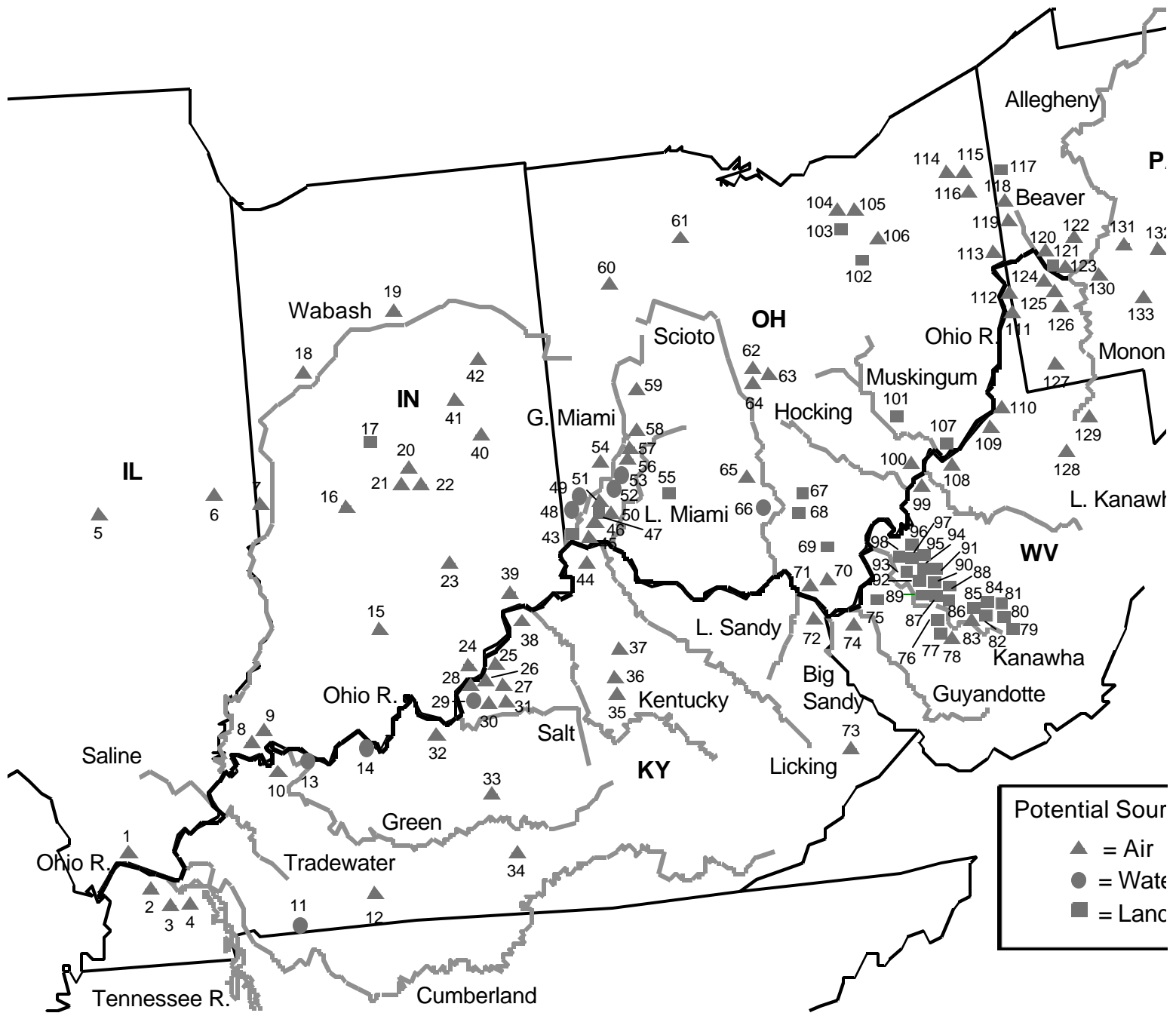
- Sources within the Ohio River TMDL segment.
- Sources upstream of the TMDL segment.
- Point sources.
- Nonpoint sources.
- Surface runoff carrying contaminated sediment.
- Resuspension of contaminated bed sediments.
- Atmospheric deposition.
- Groundwater infiltration.
- Diffusion from bed sediment pore water

Kanawha River Total Maximum Daily Load

Certain sources in the Kanawha River Basin have been identified and are described in a June 2000 report, Dioxin TMDL Development for Kanawha River, Pocatalico River, and Armour Creek, West Virginia (Limno-Tech, Inc., Ann Arbor, MI). Allocations to Kanawha Basin sources will be addressed under the Kanawha River Dioxin TMDL. The Ohio River TMDL analysis simply treats the Kanawha River as a combined dioxin load to the Ohio River. Allocations to Kanawha River sources necessary to meet water quality standards must be designed to meet Ohio River water quality standards as well. The Ohio River Valley Water Sanitation Compact requires that tributaries be of equal or better quality than the Ohio River.

Inventory of Potential and Confirmed Dioxin Sources in the Ohio River Basin

Again, little is known about specific sources of dioxin to Ohio River Basin surface waters. Most of the known contaminated sites occur in the Kanawha Basin although dioxin loads from these sites, if any, have not been determined. In a 1997 Commission report, Dioxin in the Ohio River Basin, an in-depth review of known and potential dioxin sources in the Ohio Basin was conducted. Figure 9 and Appendix B provide results of this search. Thirty-five **potential** sources, in the Ohio Basin and upstream of the Kanawha Basin, were identified. They include industries known to generate dioxin, such as cement kilns known to produce atmospheric emissions, contaminated soil sites which may or may not be contributing dioxin to surface water through erosion and runoff, etc. Of the thirty-five potential sources, seven were deemed to be “higher probability” of contributing dioxin to surface water. In addition to the listed sources, an additional Superfund site contaminated with, among other pollutants, dioxin has been discovered at ORM 10, on Neville Island in the Pittsburgh area.



Upper-Ohio River Sources

Figure 10 displays high volume dioxin sampling results from upper Ohio River surveys conducted in 1998. Dioxin concentrations are highest at ORM 20.2 (downstream of Pittsburgh) and gradually decrease in a downstream direction (with the exception of the sampling location at ORM 175.1). This might indicate a significant source(s) above the most upstream high volume sampling site, possibly in the Pittsburgh area or further upstream on the Monongahela or Allegheny Rivers. At ORM20.2, dioxin concentrations are generally highest and decrease in a downstream direction with increasing flow which suggests the possibility of point source contributions. A 2,3,7,8-TCDD concentration of 0.0244 pg/L was measured at ORM 20.2 at a low flow of 7,700 cfs. This concentration is almost twice the water quality criterion of 0.013 pg/L. Sources upstream of ORM 20 should be investigated.

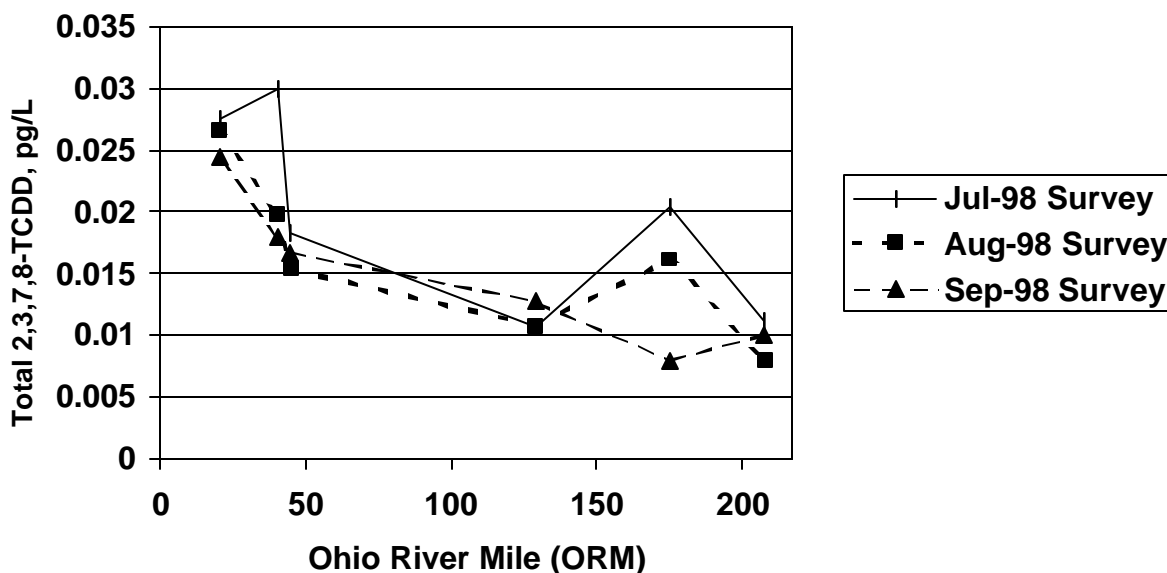


Figure 10. Upper-Ohio River Dioxin Sample Data from 1998.

In addition, there is an increase in dioxin concentration at ORM 175.1, possibly the result of a known contaminated site, or from sources on the Muskingum River. On average, the increase is 0.0035 pg/L or approximately 25 percent of the stream criterion. This increase, as an exception to an otherwise decreasing trend in a downstream direction, should be investigated further to identify sources.

Source Loadings by Category

There is no net increase of dioxin within the TMDL segment, and atmospheric deposition of 2,3,7,8-TCDD has been determined, based on limited sampling data, to be insignificant. Therefore, all important sources of dioxin that need to be accounted for are upstream of the TMDL segment, either in the Ohio River Basin upstream of ORM 264 or in the Kanawha Basin. Modeling results indicate that diffusion from pore water has been determined to be negligible. Low flow loads might typically be attributed to dry weather sources such as point sources and contributions from contaminated groundwater. Conversely, high flow loads might typically be

attributed to wet weather sources such as resuspended bed sediments and contaminated runoff. High flow related sources are much greater than from low flow sources.

Summary of Findings

- 1) Development of a total maximum daily load for the Ohio River from river mile 237.5 to 317.0 must be completed by September 2000 as required by a Federal Consent Order.
- 2) The Ohio River does not meet the water quality standard of 0.013 pg/L for dioxin. The water quality standard is designed to protect human health from long-term exposure from ingestion of contaminated water and fish.
- 3) The harmonic mean flow was selected as the appropriate critical flow condition as it best represents conditions occurring over life-time exposures to carcinogens.
- 4) Based on modeling results at the harmonic mean flow, the maximum total 2,3,7,8-TCDD load in the Ohio River is 4248 ug/day. This occurs immediately downstream of the Kanawha River. A 74 percent reduction in 2,3,7,8-TCDD would be necessary not to exceed the stream criterion. Of the total 2,3,7,8-TCDD loading at harmonic mean flow (4248 ug/day), 81 percent originates from the Kanawha River Basin while the remainder originates from the upper Ohio River Basin.
- 5) An inherent margin of safety is provided by selecting the harmonic mean flow as the critical condition over the 7Q10 low flow. At the harmonic mean flow, the reduction necessary to achieve water quality standards is 74 percent, while only 63 percent at the 7Q10 low flow.
- 6) Dioxin concentrations and loads increase with increasing flow and increasing suspended solids loads.
- 7) The largest dioxin loads for the Ohio River occur at high flows, immediately downstream of the confluence with the Kanawha River at ORM 266.
- 8) The highest flow condition simulated by the model is a one-year flood. The Ohio River flow corresponding to a one-year flood, immediately downstream of the confluence with the Kanawha River, is 267,700 cfs. This is the highest flow at which it is believed monitoring data can be used to validate modeling results.
- 9) At the one-year flood, the Ohio River daily load of 2,3,7,8-TCDD is 83,726 ug/day immediately downstream of the Kanawha River. The loading capacity necessary not to exceed the stream criterion at this flow is 8,491 ug/day, an order of magnitude less. The total daily load of 2,3,7,8-TCDD would need to be reduced 90 percent in order to meet water quality standards. At this flow, the Kanawha river contributes 55 percent of the total Ohio River dioxin loading while the upper Ohio River Basin contributes the remainder.

- 10) There is not net increase of dioxin within the TMDL segment except from that of the Kanawha River. The total daily loading of dioxin results from sources upstream of the TMDL segment.
- 11) Monitoring results indicate that atmospheric contributions of 2,3,7,8-TCDD are negligible.
- 12) Very little is known about specific sources of dioxin in the Ohio River Basin.
- 13) An upper-river dioxin survey indicates the potential presence of a significant point source(s) of 2,3,7,8-TCDD in the Ohio River upstream of ORM 20 (Pittsburgh area), and also between ORM 129 and ORM 207 (Marietta/Parkersburg area).
- 14) A Kanawha River TMDL identifies a number of sources in the Kanawha Basin.
- 15) There are significant differences in the application of states water quality standards for carcinogens for the Ohio River.

Future Areas of Study

- 1) Potential dioxin sources in the Ohio Basin upstream of ORM 20, and between ORM 129 and 175, should be investigated further. Loads from such sources should be quantified if possible.
- 2) Dioxin loads from sources identified in the Kanawha River Basin should be quantified and reduced if possible.
- 3) Studies are needed to determine the nature and extent of resuspension of contaminated sediments in the upper Ohio River.
- 4) Consistency in the application of water quality standards for dioxin (and other carcinogens having human health-based criteria) for the Ohio River needs to be achieved.
- 5) It is evident that additional dioxin congeners are typically present, each of which has a toxicity equivalence factor that allows for its expression in terms of the 2,3,7,8-TCDD congener.

DISCUSSION

Follow Up Monitoring Plan

The purpose of the follow up monitoring plan is to identify and quantify if possible specific sources of dioxin contributing to the upstream load entering the TMDL segment from the upper-Ohio River Basin. While there are suspected sources contributing dioxin to the TMDL segment from the Kanawha River Basin, this monitoring plan only addresses Ohio River sources. A Kanawha River TMDL will address sources contributing dioxin to the Ohio River.

No specific sources of 2,3,7,8-TCDD have been identified to date in the upper Ohio river Basin, even though a number of sources are suspected. Funding for this monitoring has been provided through US EPA Region 3 as a grant to the Ohio River Watershed Pollutant Reduction Program. The monitoring effort will begin in 2000 and be completed by 2001. It is anticipated that an additional follow up monitoring plan may be necessary for 2001-2002 in order to complete a thorough investigation of dioxin sources in the upper Ohio River.

Design of the following monitoring plan is based on previous dioxin monitoring and modeling efforts and presented within this report previously. Specifically, Figure 10 identifies specific locations in the upper Ohio River that should be investigated further, areas targeted by this follow up monitoring plan. In addition, modeling results suggest resuspension of contaminated sediments as a potential major source in the upper Ohio River, so this monitoring plan addresses this source also.

Monitoring to Identify Dioxin Sources in the Upper Ohio River Basin

An Upper-Ohio River longitudinal survey of dioxin, utilizing the high-volume sampling technique, was conducted in 1998. Results of that survey suggest potential sources in the Pittsburgh area between Ohio River Miles (ORM) 0 and 129, and the Marietta, OH area between ORM 129 and 175. However, no specific sources of dioxin to the Ohio River in these areas are known/quantified, even though dioxin-contaminated sites (having potential impacts) have been identified. In addition, there are a number of potential sources identified in a 1995 study conducted by ORSANCO (Figure 9). The focus of this objective is on narrowing the field of potential dioxin sources. Figure 11 is a map of high volume dioxin sampling locations discussed below which are to be included in the follow up monitoring plan.

Task 1 - Pittsburgh-Area Dioxin Source Investigation Est. Cost: \$ 123,000

This task involves narrowing the field of dioxin sources in the Pittsburgh area (ORM 0 to 129). There is one known dioxin-contaminated site along the Ohio River on Neville Island (ORM 10). In addition, there is a high density of direct discharges along the upper-Ohio River. Sampling locations are listed below and shown on Figure 11. Two rounds of high-volume sampling (at higher and lower flows) for dioxin will be completed including measurements of flow, total suspended solids (TSS), and TOC.

High-Volume Sampling Sites

Rationale

Allegheny River (near mouth)	Upstream boundary
Monongahela River (near mouth)	Upstream boundary
1. ORM 4	Upstream of contaminated site
2. ORM 10	Downstream of contaminated site
3. ORM 20	Repeat site from 1998 survey
4. Beaver River	Major trib w/potential sources
5. ORM30	Cover gaps
6. ORM 40	Repeat site from 1998 survey

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| 7. ORM 70 | Cover gaps |
| 8. ORM100 | Cover gaps |
| 9. ORM 129 | Repeat site from 1998 survey/downstream boundary |

Task 2 - Marietta-Area Dioxin Source Investigation **Est. Cost: \$ 94,000**

This task involves narrowing the field of dioxin sources in the Marietta area (ORM 129 to 207). There is one known dioxin-contaminated site at ORM 173 (at confluence with Muskingum River). Sampling locations are listed below and shown on Figure 11. Two rounds of high-volume sampling (at higher and lower flows) for dioxin will be completed including measurements of flow, total suspended solids (TSS), and TOC.

**High-Volume
Sampling Sites**

Rationale

High-Volume Sampling Sites	Rationale
9. ORM 129	Repeat site from 1998 survey/upstream boundary
10. ORM 150	Upstream Marietta urban area
11. ORM 171	Upstream contaminated site, downstream Marietta
12. Muskingum River	Potential sources exist in Muskingum basin
13. ORM 175	Repeat site from 1998; downstream contaminated site
14. ORM 185	Further downstream of contaminated site
15. ORM 207	Repeat site from 1998 survey
16. ORM 264	Upstream TMDL boundary

Task 3 - Upper Ohio River Bottom Sediment Longitudinal Survey; Est. Cost \$ 79,000

This survey will characterize Ohio River bottom sediments from Pittsburgh through the TMDL segment (ORM 0 to ORM 317). It is suspected that much of the dioxin load results from resuspension of existing contaminated sediments. The data will be used to help determine whether this assumption is correct as well as to identify hot spots. One bottom sediment sample will be collected and analyzed for dioxin every five miles from ORM 0 to ORM 317.

Task 4 - Atmospheric Dioxin Sampling **Est. Cost \$ 37,000**

Two stations in the Pittsburgh area and two stations in the Marietta area will be sampled four times (quarterly) for dioxin to determine atmospheric contributions to water.

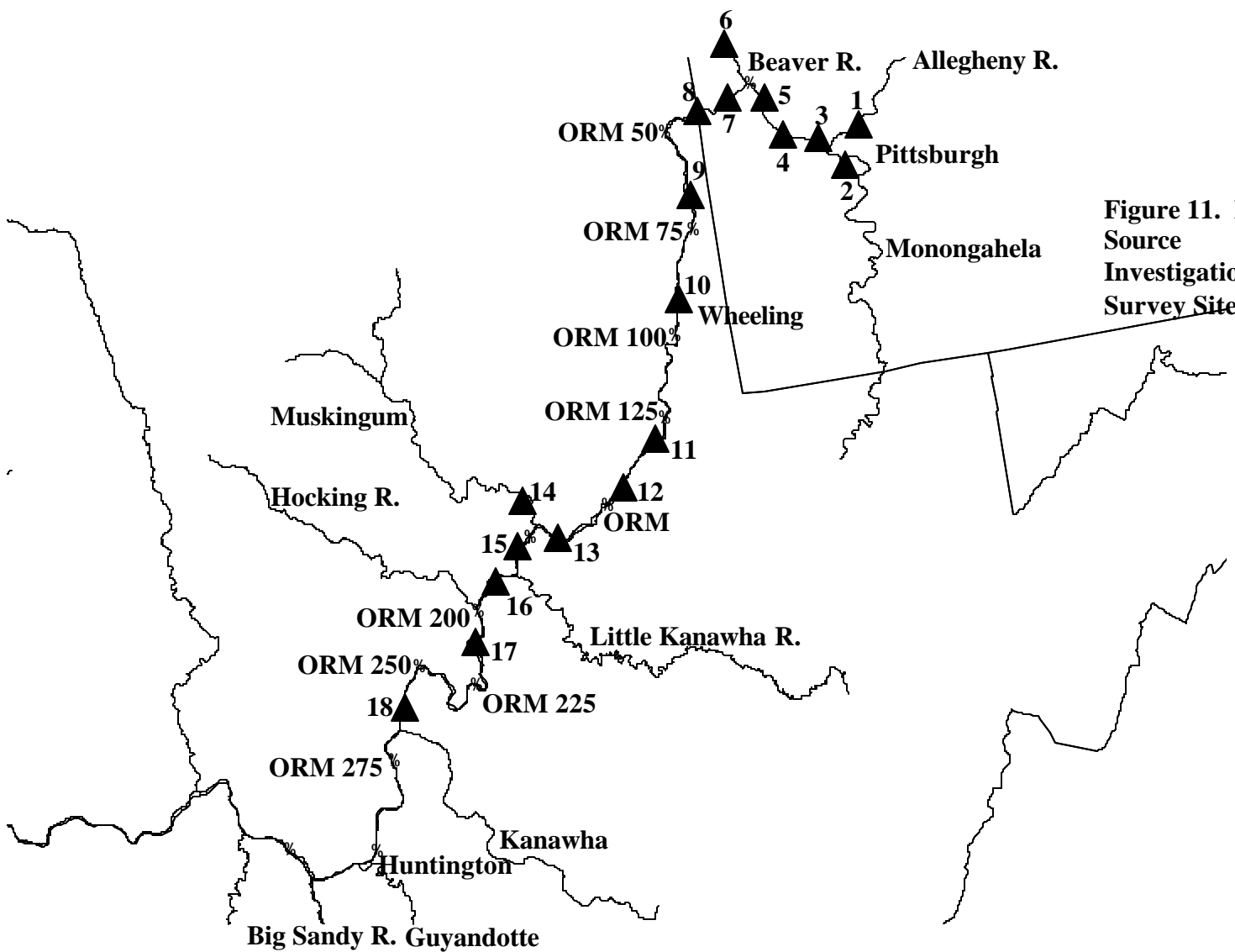


Figure 11. Dioxin Source Investigation Survey Sites.

APPENDIX A: ORSANCO High Volume Water Sampling Results

Ohio River Mile 20.2

Date sampled	NWS Flow (CFS)	2,3,7,8 TCDD pg/L (ppq)			Dioxin TEQ pg/L (ppq)		
		Dissolved	Particulate	Total	Dissolved	Particulate	Total
7/7/1998	19500	0.00365	0.0239	0.0276	0.0148	0.2190	0.23
8/4/1998	5,000	<0.00156	0.0259	0.0267	0	0	0.00
9/15/1998	7,700	<0.00092	0.0239	0.0244	0.0126	0.158	0.17
Avg.				0.0262	0.13		

Ohio River Mile 40.0

Date sampled	NWS Flow (CFS)	2,3,7,8 TCDD pg/L (ppq)			Dioxin TEQ pg/L (ppq)		
		Dissolved	Particulate	Total	Dissolved	Particulate	Total
7/8/1998	14700	0.00202	0.028	0.0300	0.0185	0.2460	0.26
8/5/1998	7300	<0.00097	0.0193	0.0198	0.0000	0.0000	0.00
9/16/1998	7800	<0.00092	0.0174	0.0179	0.0158	0.1310	0.13
Avg.				0.0226	0.13		

Ohio River Mile 44.6

Date sampled	NWS Flow (CFS)	2,3,7,8 TCDD pg/L (ppq)			Dioxin TEQ pg/L (ppq)		
		Dissolved	Particulate	Total	Dissolved	Particulate	Total
7/9/1998	21700	0.00316	0.0151	0.0183	0.0174	0.1790	0.19
8/6/1998	7,800	<0.00049	0.0152	0.0154	0.0000	0.0000	0.00
9/17/1998	7,100	<0.00072	0.0163	0.0167	0.0160	0.1170	0.13
Avg.				0.0168	0.10		

Ohio River Mile 129.0

Date sampled	NWS Flow (CFS)	2,3,7,8 TCDD pg/L (ppq)			Dioxin TEQ pg/L (ppq)		
		Dissolved	Particulate	Total	Dissolved	Particulate	Total
7/14/1998	17000	0.00248	0.0083	0.0107	0.0203	0.1070	0.12
8/11/1998	10,500	<0.00059	0.0104	0.0107	0.0264	0.1100	0.13
9/22/1998	10,100	0.00092	0.0118	0.0127	0.0085	0.1110	0.11
Avg.				0.0114	0.12		

Ohio River Mile 175.1

Date sampled	NWS Flow (CFS)	2,3,7,8 TCDD pg/L (ppq)			Dioxin TEQ pg/L (ppq)		
		Dissolved	Particulate	Total	Dissolved	Particulate	Total
7/15/1998	34600	0.00103	0.0194	0.0204	0.0088	0.2830	0.29
8/12/1998	19,100	<0.00149	0.0155	0.0162	0.0000	0.1580	0.15
9/23/1998	14,200	<0.00025	0.0078	0.0079	0.0075	0.1000	0.10
Avg.				0.0149	0.18		

Ohio River Mile 207.7

Date sampled	NWS Flow (CFS)	2,3,7,8 TCDD pg/L (ppq)			Dioxin TEQ pg/L (ppq)		
		Dissolved	Particulate	Total	Dissolved	Particulate	Total
7/16/1998	32500	0.00166	0.0095	0.0112	0.0198	0.2340	0.25
8/13/1998	20,500	<0.00032	0.0078	0.0080	0.0223	0.2200	0.24
9/24/1998	12,000	0.00350	0.0065	0.0100	0.0207	0.1310	0.15

7/15/1997	759	5,000	0.00969	0.0885	0.0982	0.0122	0.1969	0.20
8/19/1997	3,153	5,000	0.01780	0.1050	0.1228	0.0242	0.2310	0.23
9/23/1997		3700	0.02000	0.1140	0.1340	0.0230	0.2061	0.22
10/22/1997		3200	0.01160	0.1750	0.1866	0.0150	0.2865	0.30
6/17/1998		44900	0.01580	0.4470	0.4628	0.0526	1.4400	1.49
11/2/1998		3600	0.01860	0.1500	0.1686	0.0238	0.2490	0.27
Average		11,567	0.01375	0.1693	0.1831	0.0231	0.4233	0.44

Ohio River Mile 264

Date sampled	Flowsed Flow (CFS)	NWS Flow (CFS)	2,3,7,8 TCDD pg/L (ppq)			Dioxin TEQ pg/L (ppq)		
			Dissolved	Particulate	Total	Dissolved	Particulate	Total
7/16/1997	16,133	19000	0.00271	0.0140	0.0167	0.0184	0.3176	0.3360
8/20/1997	82,121	62700	0.00202	0.0098	0.0118	0.0152	0.5160	0.5312
9/24/1997		14500	<0.00099	0.00802	0.0085	0.0131	0.2683	0.2814
6/18/1998		93700	<0.00260	0.0697	0.0710	0.0473	1.7195	1.7668
11/3/1998		9100	0.00251	0.00426	0.0068	0.0119	0.0888	0.1007
Average		47475	0.00181	0.0254	0.0270	0.0235	0.7054	0.7289

Ohio River Mile 281.5

Date sampled	Flowsed Flow (CFS)	NWS Flow (CFS)	2,3,7,8 TCDD pg/L (ppq)			Dioxin TEQ pg/L (ppq)		
			Dissolved	Particulate	Total	Dissolved	Particulate	Total
7/17/1997	18,557	21,300	0.00536	0.0323	0.0377	0.0165	0.2965	0.3130
8/21/1997	69,105	68,800	0.00334	0.0443	0.0476	0.0135	0.8920	0.9055
9/25/1997		17600	<0.00086	0.0306	0.0310	0.0073	0.2469	0.2542
6/19/1998		175400	0.00714	0.1360	0.1364	0.0466	1.2900	1.3366
11/4/1998		15900	0.00801	0.0236	0.0240	0.0183	0.1010	0.1193
Average		70,775	0.00407	0.0608	0.0632	0.0210	0.6814	0.7024

Ohio River Mile 302.9

Date sampled	Flowsed Flow (CFS)	NWS Flow (CFS)	2,3,7,8 TCDD pg/L (ppq)			Dioxin TEQ pg/L (ppq)		
			Dissolved	Particulate	Total	Dissolved	Particulate	Total
7/18/1997	16,829	20,400	0.00586	0.0294	0.0353	0.0118	0.1996	0.2114
8/22/1997	47,885	61,300	<0.00040	0.0440	0.0442	0.0117	0.4830	0.4947
9/26/1997		21800	0.00485	0.0180	0.0229	0.0156	0.1169	0.1325
6/20/1998		103900	0.00712	0.1600	0.1671	0.0529	0.7330	0.7859
11/5/1998		17600	0.00649	0.0190	0.0255	0.0164	0.0909	0.1073
Average		51,850	0.00594	0.0629	0.0674	0.0230	0.3831	0.4061

Guyandotte River Mile 1.1

Date sampled	Flowsed Flow (CFS)	Flow (CFS)	2,3,7,8 TCDD pg/L (ppq)			Dioxin TEQ pg/L (ppq)		
			Dissolved	Particulate	Total	Dissolved	Particulate	Total
12/16/1998		1,200	<0.00018	<0.00083	<0.00101	0.0078	0.2480	0.2558
3/17/1999		6,600	0.00097	0.0191	0.0201	0.0046	0.2930	0.2976
Average			0.00053					

